

Drying characteristics and degradation kinetics in some parameters of goji berry (*Lycium Barbarum* L.) fruit during hot air drying

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Received: 24 August 2020; Accepted: 07 October 2020; Published: 01 February 2021

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PAPER

Abstract

Drying kinetics, color properties, water-soluble vitamins, antioxidant capacity, total phenolic content, and thermal degradation kinetics of bioactive compounds in goji berries were investigated. Drying experiments were conducted at 50°C, 60°C, and 70°C. Page model was determined as the best model to predict experimental moisture ratio for all temperatures. Increment in drying temperature increased effective moisture diffusivity and drying rate values. Vitamins C and B₆, antioxidant activity and total phenolic content were significantly reduced by drying. Thermal degradation of vitamins C and B₆, antioxidant capacity and total phenolic content were found to fit the first-order kinetic model.

Keywords: antioxidant capacity, degradation kinetics, drying kinetics, goji berry, total phenolic content, water-soluble vitamins

Introduction

Goji berry (*Lycium barbarum* L.), which belongs to *Solanaceous* family, is grown in China, Tibet, and some regions of Asia. Goji berry is primarily found in East Asia and grown particularly in Japan, South Korea, and South China (Gao *et al.*, 2017). *Lycium barbarum* L. is a deciduous woody shrub, mostly thorny, that grows 1–4 m in height (Griffiths and Huxley, 1992). Fruits are two-chambered, mostly orange-red in color, juicy, and fleshy (Chen *et al.*, 2018). Ripe goji berries are 3–10 mm in diameter, 6–20-mm long, and have oblong or ellipsoid shape (Gao *et al.*, 2017).

Goji berry contains a high amount of anthocyanin (Cui *et al.*, 2011), carotenoids (lycopene, zeaxanthin dipalmitate, beta-carotene, zeaxanthin, and lutein), vitamins (tocopherol, glucopyranosyl ascorbic acid, and ascorbic acid), betaine, fatty acids, and peptidoglycans (Islam *et al.*, 2017). Fatty acids commonly found in goji berry are linoleic, oleic,

and palmitic acids (Cossignani *et al.*, 2018). The fruit also includes organic acids such as malic, citric, shikimic, and fumaric acids (Mikulic-Petkovsek *et al.*, 2012), monosaccharides, which are mannose, rhamnose, galactose, xylose, arabinose, and glucose, 18 amino acids, and galacturonic acid (Amagase and Farnsworth, 2011). Owing to bioactive substances and healthy functions, goji berries are popular in the western world (Bertoldi *et al.*, 2019).

In traditional Chinese herbal medicine, goji berry has been used as a supplement for more than 2000 years (Burke *et al.*, 2005). It is used to protect the liver, kidneys, and eyes, strengthen the eyesight (Shan *et al.*, 2011), and reduce serum lipids and blood glucose levels. Also, Goji berry has other health-promoting effects such as anti-radiation, immune-enhancing, anti-fatigue, and anti-aging effects, stimulating hematopoiesis, and treating male infertility (Luo *et al.*, 2004; Tian *et al.*, 2013).

Drying is a protection technique that is widely applied to fresh products. Dehydration prolongs stability of fruits and vegetables by decreasing water content and minimizing physicochemical changes and microbial growth (Tepe and Tepe, 2020). Besides, the drying process protects valuable foods under effective conditions, prolongs shelf life, and reduces storage, transportation, and packaging costs because of decrement in the volume and weight of food products (Önal *et al.*, 2019). One of the most important steps in the food processing industries is the dehydration process.

Sun drying is a preferred method because it is economical and does not require investment, but it is a disadvantageous method due to microbial reliability and loss in quality such as color and aroma (Göztok and İçier, 2017). Convective drying is one of the most used drying methods to protect agricultural products compared to other drying methods because it is simple and low costing. On the contrary, this method causes changes in sensory properties and nutritional values (Orikasa *et al.*, 2014). The convective drying can be used as an alternative method instead of conventional (sun) drying. It has more advantages than conventional drying in terms of preventing microbial contamination, component protection, and involving lower drying time (Lewicki, 2006). Adiletta *et al.* (2015) and Fratianni *et al.*, (2018) studied goji berry drying, but no data are available in literature about drying characteristics, degradation kinetics of water-soluble vitamins, antioxidant capacity (AC), and total phenolic content (TPC) of dried goji berry fruit.

Absence of data on drying characteristics and degradation of some bioactive compounds can be regarded as a gap in the drying process of goji berry fruit. In this context, determining drying characteristics and degradation of some bioactive compounds can be useful for the designing of drying process. Thus, the aims of this study are to: determine the drying characteristics of goji berry fruit at 50°C, 60°C, and 70°C, examine the influence of drying process on contents of vitamins C and B₆, antioxidant capacity and total phenolic content of goji berries, and calculate the degradation kinetics of these bioactive compounds.

Materials and Methods

Materials and sample preparation

Goji berry fruits, of NQ1 variety, were obtained from Redlife in the Çivril district of Denizli province of Turkey. Geographical location of Denizli is between 28°30'–29°30' east meridians and 37°12'–38°12' north parallels and is located in the Aegean region of Turkey. The fruits were carefully collected in July 2019 from 10 randomly selected plants. Fresh fruits were washed to remove any foreign material and kept at –18°C before analysis.

Method

Drying process of samples

Goji berry samples were dried in a tray drying cabinet (Yücebaş Makine Tic. Ltd. Şti., İzmir, Turkey). Dryer comprised an electronic proportional controller (EUC442 model, ENDA, Turkey), an electric heater, and a centrifugal fan to provide airflow. The dryer's internal size was 70 cm × 55 cm × 100 cm, the range of workable temperature was 40–120°C, and the range of workable relative humidity was 20%–95%. Three different drying air temperatures were used in the experiments: 50°C, 60°C, and 70°C. The cabinet was heated for 1 h before the start of drying process to reach a constant temperature; and 200 g of samples were uniformly placed on the drying tray. The drying process was performed up to the targeted dry matter content at a relative humidity of 20% and air velocity of 2 m/s. The drying experiments were performed in triplicate and weighed at certain time intervals with a 0.001 g precision digital scale.

Drying characteristics of goji berry fruit

Empirical models are more useful because theoretical drying models are complicated and the former models offer a direct relationship between drying time and moisture content (Moradi *et al.*, 2020). Thin-layer drying models have great significance in designing the best drying conditions.

Moisture ratio (MR) must be calculated by M_i , M_t , and M_e values to choose the best model.

$$MR = \frac{M_t - M_e}{M_i - M_e} \quad (\text{Eq. 1})$$

where

M_i : initial moisture content of samples (g water/g dry matter);

M_t : moisture content at any time (g water/g dry matter);

M_e : equilibrium moisture content (g water/g dry matter).

However, if the equilibrium moisture content (M_e) is very low than M_t and M_i , it can be neglected and Equation 2 is used (Yousefi *et al.*, 2013):

$$MR = \frac{M_t}{M_i} \quad (\text{Eq. 2})$$

Drying rate (DR) was determined using Equation 3:

$$DR = \frac{M_{t+\Delta t} - M_t}{\Delta t} \quad (\text{Eq. 3})$$

where

$M_{t+\Delta t}$: moisture content at time difference;

Δt : time difference between two measuring points.

The relation between predicted and experimental data of goji berry fruits dried at different drying temperatures is explained with root mean square error (RMSE), reduced chi-square (χ^2), and determination coefficient (R^2). RMSE is a statistical parameter that expresses deviation between experimental and predicted values. The best equation predicting experimental data is determined accordingly with lower RMSE and χ^2 and higher R^2 values. The chi-square (Equation 4) and RMSE (Equation 5) values were calculated as follows:

$$\chi^2 = \frac{\sum_{i=0}^N (MR_{pre,i} - MR_{exp,i})^2}{N - n} \quad (\text{Eq. 4})$$

$$RMSE = \left[\frac{1}{N} \sum_{i=0}^N (MR_{pre,i} - MR_{exp,i})^2 \right]^{1/2} \quad (\text{Eq. 5})$$

where

$MR_{pre,i}$: predicted MR;

$MR_{exp,i}$: experimental MR;

N : number of observation data;

n : constants of thin layer drying models.

MATLAB software was used to calculate thin-layer modeling and for statistical analyses.

Determination of effective moisture diffusivity and activation energy in hot air drying

Fick's diffusion equation described the drying characteristics of biomaterials. Crank (1975) suggested a solution to this equation to be used for spherical products. Equation 6 is recommended for spherical products, provided that there is no shrinkage and constant effective diffusivity (Doymaz, 2006):

$$MR = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-n^2 \pi^2 D_{eff}}{r^2}\right) \quad (\text{Eq. 6})$$

where

D_{eff} : effective moisture diffusivity (m^2/s)

r : arithmetical average of radius of samples at measured intervals (m).

Equation 6 can be reduced (Saravacos and Raouzeos, 1986) and a new equation is provided below:

$$\ln(MR) = \ln\left(\frac{6}{\pi^2}\right) - \left(\frac{\pi^2 D_{eff}}{r^2} t\right) \quad (\text{Eq. 7})$$

Equation 8 shows a straight line with a slope provided in the plot:

$$\text{Slope} = -\frac{\pi^2}{r^2} D_{eff} \quad (\text{Eq. 8})$$

The Arrhenius equation of hot air-drying process was used for calculation of activation energy (Fang *et al.*, 2009):

$$D_{eff} = D_0 \exp\left(\frac{-E_a}{RT}\right) \quad (\text{Eq. 9})$$

where

R : universal gas constant [8.314 J/mol (K) or 1.987 cal/mol (K)];

T : absolute temperature (K);

E_a : activation energy (kJ/mol or kcal/mol);

D_0 : pre-exponential constant (m^2/s).

After regulation of natural logarithm in Equation 8, Equation 9 can be written as follows:

$$\ln D_{eff} = \ln D_0 - \frac{E_a}{RT} \quad (\text{Eq. 10})$$

Natural logarithm of effective moisture diffusivity versus $1/T$ gives a straight line with a slope that represents activation energy.

Analysis of water-soluble vitamins

An extraction method proposed by Donmez (2015) was used for analysis of water-soluble vitamins. To determine water-soluble vitamins, a sample of 5 g of goji berries was taken, and after homogenization with distilled water (1:9, w:v), the homogenate was centrifuged at 4500 rpm for 10 min (Core NF 800R). The supernatant obtained from centrifugation was filtered using a 0.45- μ m filter to be injected into a high-pressure liquid chromatography (HPLC) column.

Using a micro syringe, 20 μ L of filtrate was injected into the HPLC column. Mobile phase consisted of 0.1 M HPLC grade KH_2PO_4 at pH 7.

The HPLC device (Shimadzu), in which analysis of water-soluble vitamins was performed, consisted of column oven (Shimadzu CTO-20A, Japan), pump (Shimadzu LC-20AD, Japan), degasser (Shimadzu DGU-20A3, Japan), photodiode array (PDA) detector, and HPLC software in a computer. The column used in the analysis was ACE C18 column (7.8 \times 300 mm), column temperature was 25°C, and the flow rate of mobile phase was 0.8 mL/min (isocratic). Wavelengths used in analysis were 254 nm, 261 nm, 324 nm, and 234 nm for ascorbic acid, niacin, pyridoxine, and thiamine, respectively. Analysis was performed in triplicate.

A calibration curve of different concentrations of stock solutions (5, 10, 25, 50, 75, and 100 ppm) with high R^2 (0.9999) was obtained. The content of water-soluble vitamins was calculated by the equation obtained from the calibration curve.

Analysis of antioxidant capacity and total phenolic content

The AC and TPC analysis was carried out using the methanolic extraction method proposed by Otağ (2015). A sample of 5 g of goji berries was mixed with 45 mL of 90% methanol and homogenized using a laboratory blender. The homogenate was centrifuged at a speed of 4500 rpm for 10 min. After centrifugation, supernatants were collected and filtered using a filter paper.

The TPC analysis was performed according to Singleton and Rossi (1965) with modifications. In this analysis, 1500 μL Folin–Ciocalteu solution (10% v/v) was added into 300 μL of extract and the mixture was kept in a dark place for 3 min. Then 1200 μL aqueous 7.5% Na_2CO_3 was added into the mixture. The final mixture was incubated for 2 h at room temperature in a dark place. After incubation, the absorbance measurement of the samples was carried out at a wavelength of 760 nm using spectrophotometer (T80, PG Ins., UK.). Analysis was carried out in triplicate, and TPC was expressed as mg/100 g gallic acid equivalent (GAE) dry weight (DW).

The AC analysis was carried out using the method suggested by Thaipong *et al.* (2006) with modifications. Here, 150 μL of extracts and 2850 μL of DPPH methanolic solution (absorbance value: 1.1 at a wavelength of 515 nm) were mixed. Absorbance of samples was measured at a wavelength of 515 nm using spectrometer after 60 min incubation in a dark place at room temperature. Each sample was analyzed in triplicate and AC was expressed as mmol Trolox equivalent (TE)/g DW.

Color measurement

Reflectance color value of goji berry skin was measured by using Hunter Lab Color Miniscan XE (45/0-L, USA). The samples were placed on a white background and the measurement was performed by covering with a transparent glass. The highest color difference (ΔE) was calculated using Equation 11 (Horuz *et al.*, 2017):

$$\Delta E = \sqrt{(L_0 - L)^2 + (a_0 - a)^2 + (b_0 - b)^2} \quad (\text{Eq. 11})$$

Calculation of kinetic parameters

The following equation (Equation 12) was used as a general equation to describe the reaction rate of the compounds that are degraded or formed by Labuza (1984):

$$\frac{dc}{dt} = k[C]^m \quad (\text{Eq. 12})$$

For the zero-order kinetic model, equation can be written as follows:

$$C = C_0 - Kt \quad (\text{Eq. 13})$$

If Equation 13 is integrated and $m = 1$, then Equation 14 is written as follows:

$$\ln C = \ln C_0 - kt \quad (\text{Eq. 14})$$

where

$\ln C$: natural logarithm of the residual vitamins C and B complex, TPC, and AC;

$\ln C_0$: initial content of vitamins C and B complex, TPC, and AC]

k : rate constant (1/h);

t : time.

Temperature dependence of vitamins C and B complex, TPC, and AC can be calculated using Equation 15 (Labuza and Riboh, 1982):

$$k = k_0 x e^{-\frac{E_a}{RT}} \quad (\text{Eq. 15})$$

When Equation 15 is regulated, Equation 16 is written as follows:

$$\ln k = \left(-\frac{E_a}{R}\right) x \left(\frac{1}{T}\right) + \ln k_0 \quad (\text{Eq. 16})$$

where

k_0 : frequency factor (1/h);

R : universal gas constant [8.314×10^{-3} kJ/mol (K) and 1.987×10^{-3} kcal/mol (K)];

T : absolute temperature (K);

E_a : activation energy (kcal/mol or kJ/mol).

Quotient indicator (Q_{10}) expresses temperature-dependence of reaction rate and is calculated using Equation 17 (Labuza and Schimidl, 1985):

$$Q_{10} = \left(\frac{k_2}{k_1}\right)^{\left(\frac{10}{T_2 - T_1}\right)} \quad (\text{Eq. 17})$$

Half-life time, time required for half of concentration, for each temperature is calculated using Equation 18 for first-order kinetics (Labuza, 1984):

$$t_{1/2} = -\ln(0.5) x \frac{1}{k} = 0.693 x \frac{1}{k} \quad (\text{Eq. 18})$$

Time taken by the compound, or quality criterion, to lose 90% of its quality is expressed as D and is calculated for first-order kinetics as follows (Equation 19):

$$D = 2.303 x \frac{1}{k} \quad (\text{Eq. 19})$$

Statistical analysis

SPSS 22.0 software (IBM Corporation, Armonk, NY) was used for statistical analysis and expressed as mean \pm standard deviation (SD). Analysis of variance (ANOVA) was used to evaluate differences between treatments with the significance level $P = 0.05$. Differences between groups were determined using the Duncan test.

Results and Discussion

Drying characteristics of goji berry fruits during hot air drying

The drying rate and moisture ratio values of goji berries during hot air drying are presented in Figure 1. Drying time and drying rate of goji berry fruits were significantly affected by drying temperature, and it is clearly seen that drying rate increases with the increment in drying temperature.

Drying time decreased depending on the increment in temperature, so drying time was found to be 24 h at 50°C, 19 h at 60°C, and 9 h at 70°C. Adiletta *et al.* (2015) determined drying time as 21 h at 60°C for hot air-drying treatment of goji berries. Fratianni *et al.* (2018) dried goji berry fruits in a convective dryer and the drying process was finished in 45 h at 50°C, 21 h at 60°C, and 12 h at 70°C, and the velocity of air was 2.1 m/s. It could be that the increment in drying rate with increase in temperature might be due to the increase in heat transfer coefficient. The results of this study were similar to the results of the studies examined in literature.

Mathematical models used in modeling the drying process, constants, and the statistical data of mathematical models are listed in Table 1. Demiray *et al.* (2017) reported that the lower RMSE and χ^2 and the higher R^2 values are required for determining the best model. As seen in Table 1, the Page (1949) model is the best

model predicting experimental moisture ratio of goji berry fruits for all drying temperatures (50°C, 60°C, and 70°C), with the lowest RMSE and χ^2 and the highest R^2 values.

Effective moisture diffusivity and activation energy of goji berry fruits during hot air drying

The effective moisture diffusivity (D_{eff}) and activation energy (E_a) values of goji berry fruits are presented in Table 2, and the D_{eff} values were calculated in the range of 2.98×10^{-8} – 1.04×10^{-8} m²/s. Effective moisture diffusivity is a useful indicator of dehydration effectiveness (Chen *et al.*, 2016). When compared with other drying temperatures, the highest D_{eff} value was determined in the drying process conducted at 70°C. Increase in the D_{eff} value means the moisture content in goji berry samples is evaporated more easily. As understood from Equation 9 mentioned above, it is a known fact that the drying temperature is an important factor affecting the D_{eff} value.

No mention of D_{eff} value during the drying of goji berry fruits with hot air was found in literature. Senadeera *et al.* (2014) found D_{eff} values in the range of 1.32×10^{-6} – 1.34×10^{-6} m²/h because of the drying process executed on different types of grapes at 50°C, 0.5 m/s air velocity, and 20% moisture content. Chen *et al.* (2016) carried out hot air drying of wine grapes, grown in Canada, between 25°C and 80°C and determined the D_{eff} value at 25°C and 80°C as 0.05×10^{-10} m²/s and 0.49×10^{-10} m²/s, respectively, at MR = 0.2. They observed that the D_{eff} values increased 10 times with increase in temperature from 25°C to 80°C. Dong *et al.* (2013) studied the drying process of grapes at 30°C, 35°C, 40°C, and 45°C and found that the D_{eff} value was higher at the highest temperature. In other words, the D_{eff} value increases with increase in drying temperature, and the data examined in literature support our study.

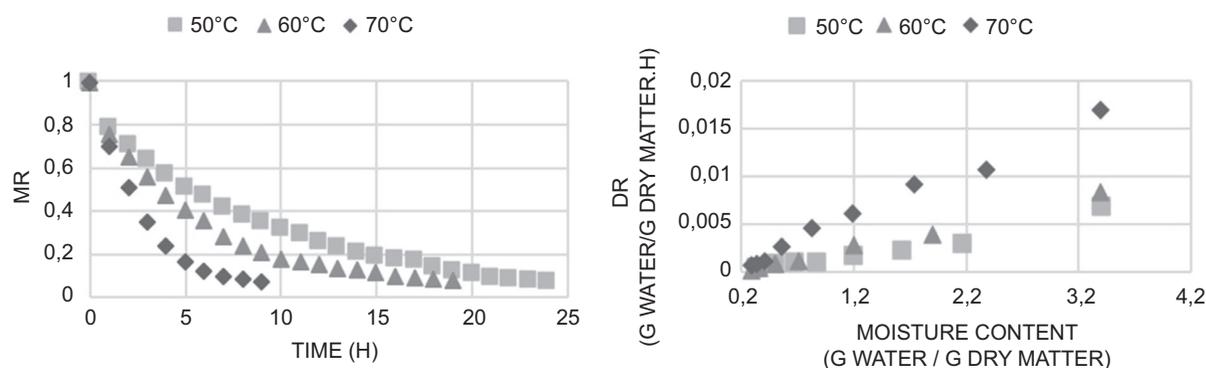


Figure 1. Moisture ratio and drying rate of goji berries during hot air drying.

Table 1. Thin-layer mathematical models, model constants, and statistical parameters of thin-layer drying curves.

Model Names and References	Model	Temperature	Model Constants			χ^2	RMSE	R ²
Lewis / Lewis (1921)	exp(-kt)	50°C	k = 0.1186			0.001344007	0.03592	0.9793
		60°C	k = 0.1737			0.001277711	0.03484	0.9819
		70°C	k = 0.3450			0.000251669	0.01505	0.9977
Page / Page (1949)	exp(-kt ⁿ)	50°C	k = 0.1812	n = 0.8161		0.000264861	0.01561	0.9962
		60°C	k = 0.2508	n = 0.8107		0.000165378	0.01220	0.9979
		70°C	k = 0.3574	n = 0.9716		0.000290322	0.01524	0.9979
Henderson and Pabis / Henderson and Pabis (1961)	aexp(-kt)	50°C	k = 0.1075	a = 0.9150		0.000576501	0.02303	0.9918
		60°C	k = 0.1607	a = 0.9316		0.000866761	0.02793	0.9890
		70°C	k = 0.3438	a = 0.9964		0.000316013	0.01590	0.9977
Logaritmik / Doymaz (2011)	aexp(-kt) + c	50°C	k = 0.1341	a = 0.8742	c = 0.07044	0.000666050	0.02421	0.9910
		60°C	k = 0.2094	a = 0.8951	c = 0.07613	0.000296302	0.01587	0.9964
		70°C	k = 0.4267	a = 0.9425	c = 0.07490	0.000811922	0.02384	0.9948
Wang and Singh / Wang and Singh (1978)	1 + at + bt ²	50°C	a = -0.09269	b = 0.002374		0.003999604	0.06066	0.9433
		60°C	a = -0.13020	b = 0.004536		0.004329174	0.06242	0.9450
		70°C	a = -0.26180	b = 0.018240		0.001641672	0.03624	0.9880
Parabolic / Bi et al. (2015)	a + bt + ct ²	50°C	a = 0.8701	b = -0.07149	c = 0.001653	0.001539746	0.03681	0.9800
		60°C	a = 0.8800	b = -0.10560	c = 0.003485	0.002166198	0.04291	0.9754
		70°C	a = 0.9556	b = -0.24320	c = 0.016610	0.001492261	0.03232	0.9917

RMSE, root mean square error.

Table 2. Effective moisture diffusivity and activation energy of goji berry fruit.

Temperature	D _{eff} (m ² /s)	E _a (kJ/mol)	E _a (kcal/mol)
50°C	1.04 × 10 ⁻⁸		
60°C	1.31 × 10 ⁻⁸	48.37	11.56
70°C	2.98 × 10 ⁻⁸		

The Arrhenius-type relation between D_{eff} and 1/T is presented in Figure 2. The E_a values of goji berry fruits were found to be 48.37 kJ/mol and 11.56 kcal/mol. In literature, no activation energy data for hot air drying of goji berry fruits were found. When compared with similar berry fruits dried with hot air, Vega-Galvez *et al.* (2009) found E_a = 48.34 kJ/mol in blueberries. In another study done on hot air drying, Abdulla (2012) found E_a = 51.31 kJ/mol for golden fruits. López *et al.* (2010) and Shi *et al.* (2008) reported the E_a values of blueberry as 57.85 kJ/mol and 61.2 kJ/mol, respectively. Although the values found in some studies are similar to the values found in our study, others were higher. Differences between the results of the current study and other studies, in which other fruits were used, may be due to different factors such as different fruit structures, temperature, airflow rate, and relative humidity.

Effect of drying process on water-soluble vitamins, total phenolic content, and antioxidant capacity

Effects of drying on water-soluble vitamins of goji berries are provided in Table 3. Carr and Frei (1999) indicated that vitamin C easily scavenges nitrogen species and reactive oxygen and thereby may prevent oxidative damage to nontrivial biological macromolecules such as proteins, lipids, and DNA. It is extremely important to maintain vitamin C during the drying process or to carry out this process with minimal loss; however, vitamin C is significantly affected by the drying process. In this study, value of vitamin C in fresh goji berries was found to be 112.75 ± 2.23 mg/100 g DW. Donno *et al.* (2015) found the concentration of vitamin C in goji berries to be 42 mg/100 g FW (fresh weight). The United States Department of Agriculture (USDA) has found the amount of vitamin C in dried goji fruit to be 48.4 mg/100 g (Koçyiğit and Sanlier, 2017). When compared with literature, it could be said that goji berries grown in Turkey are rich in vitamin C. There are statistical losses in values of vitamin C at all drying temperatures (P < 0.05). Vitamin C values at 50°C, 60°C and 70°C were determined as 39.45 ± 2.21, 26.48 ± 1.16 and 21.87 ± 0.971 mg/100 g DW, respectively. Since vitamin C has low stability against heat treatments, it is established as

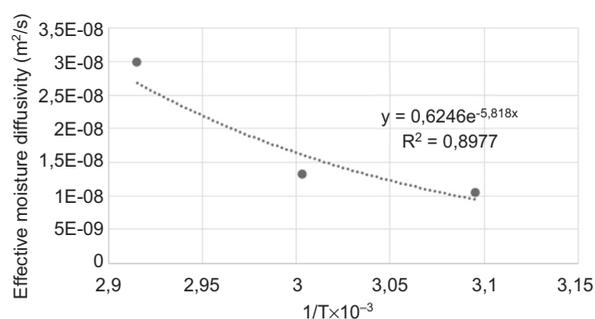


Figure 2. The Arrhenius-type relation between effective moisture diffusivity and $1/T$.

a quality index in foods during the processing (DiScala and Crapiste, 2008). Besides kinetic parameters, vitamin C may be a significant quality parameter in goji berries' drying process. López *et al.* (2010) reported that there were significant loss in vitamin C values of blueberries at all drying temperatures, and the highest loss was 92% at 80°C. In a detailed review on ascorbic acid, Santos and Silva (2008) stated that a significant loss in ascorbic acid was seen due to hot air drying of fruits and vegetables. They even stated that no vitamin C was left in some drying processes applied on tomatoes over 100°C. Other studies (Araya-Farias *et al.*, 2011; Kadakal *et al.*, 2017) have demonstrated that the hot air-drying process significantly reduces the amount of vitamin C.

In our study, the amount of vitamin B complex was analyzed in fresh goji berry fruits and the kinetic data were obtained during the drying process. The amount of pyridoxine (B_6) in fresh goji berries was determined as 2.19 ± 0.046 mg/100 g DW but thiamine, riboflavin, and niacin were not detected. Right after hot air-drying process at different temperatures, amount of pyridoxine was determined as 0.937 ± 0.055 , 0.681 ± 0.061 , and 0.49 ± 0.034 mg/100 g DW at 50°C, 60°C, and 70°C, respectively. The highest loss appears to be in the drying process at 70°C.

Ryley and Kajda (1994) stated that loss in the values of water-soluble vitamins was observed with the effect of heat treatment in various foods. In consequence of drying at different temperatures, an important decrease in the amount of pyridoxine was observed in goji berries. Decrease in the amount of water-soluble vitamin B_6 increases with the increment in drying temperature.

Effects of hot air drying on total phenolic content and antioxidant capacity of goji fruits are presented in Table 3. The TPC and AC values of fresh goji berries were found as 1838.43 ± 37.47 mg/100 g DW and 0.077 ± 0.002 mmol TE/g DW, respectively. Islam *et al.* (2017) determined the TPC value of red goji berry fruits as 217–448 mg GAE/100 g. Ban *et al.* (2015) determined the TPC value of fresh goji berries in the range of 449.92–450.48 mg GAE/kg FW. Zhang *et al.* (2016) determined the TPC values of goji berry fruits in the range of 5840–7340 mg GAE/100 g FW. Pedro *et al.* (2018) investigated TPC by extraction of goji berry fruits in different concentrations of methanol and found it in the range of 1052.53–1736.36 mg GAE/100 g. The TPC of goji berry fruits because of drying processes at 50°C, 60°C, and 70°C was determined to be 491.00, 450.17, and 404.45 mg GAE/100 g DW, respectively. Islam *et al.* (2017) and Zhang *et al.* (2016) determined the AC value of red goji berry fruits as 16.07–17.47 mg μ mol TE/g and 77.41–85.46 μ MTE/g FW, respectively. Pedro *et al.* (2018) found the AC values of goji berry in the range of 0.94–1.51 mmol TE/100 g. Mikulic-Petkovsek *et al.* (2014) stated that a significant difference in the content of fruits is seen when grown at different locations. The compositional difference seen in the same varieties of fruits and vegetables is influenced by numerous factors such as environmental conditions of the region where the product is grown, especially soil quality, cultivation technique and cultural measures, maturity level, transportation and storage, and so on (Gökkür and Çelik, 2016). The reason why our results are different from those found in literature may be due to the reasons explained above.

Table 3. Effect of drying process on vitamins C and B_6 , total phenolic content, and antioxidant capacity of goji berries.

	Vitamin C*	Loss percentage (%)	Pyridoxine (B_6)*	Loss percentage (%)	TPC**	Loss percentage (%)	AC**	Loss percentage (%)
Fresh	112.75 ± 2.23^a	0	2.19 ± 0.046^a	0	1838.43 ± 37.47^a	0	0.077 ± 0.002^a	0
50°C	39.45 ± 2.21^b	65.03	0.937 ± 0.055^b	56.56	491.00 ± 7.96^b	73.29	0.017 ± 0.001^b	77.92
60°C	26.48 ± 1.16^c	76.84	0.681 ± 0.061^c	69.04	450.17 ± 8.26^b	75.51	0.014 ± 0.001^{bc}	81.82
70°C	21.87 ± 0.971^d	80.5	0.492 ± 0.034^c	77.48	404.45 ± 6.89^c	78	0.011 ± 0.001^c	85.71

*Vitamins C and B_6 was expressed as mg/100 g DW.

**TPC was expressed as mg GAE/100 g DW, AC was expressed mmol TE/g DW.

***Different letters in the same column are significantly different values ($P < 0.05$).

TPC, total phenolic content; GAE, gallic acid equivalent; TE, trolox equivalent; DW, dry weight.

Color properties of goji berry fruit during hot air drying

Color properties of fresh and dried goji berries were presented in Table 4. When compared with initial L^* , a^* , and b^* values of goji fruits, values were significantly decreased due to drying process ($P < 0.05$) and the lowest L^* , a^* , and b^* values were obtained at 70°C. ΔE indicates differences between colors of samples (Horuz *et al.*, 2017). The ΔE value of dried goji fruits depends on drying conditions and ranges from 10.87 to 13.91. The highest ΔE was obtained from the goji berry fruits dried at 70°C.

Kinetic parameters of vitamins C and B6

To the best of our knowledge, vitamin C degradation in the hot air-drying process of goji berries was investigated for the first time in this study. Thermal degradation of vitamin C in goji berries is shown in Figure 3; its content in fully dried goji berries is found to fit the first-order kinetic model. It is stated by Gamboa-Santos *et al.* (2014), Hiwilepo-van Hal *et al.* (2012), Kadakal *et al.* (2017), and Wang *et al.* (2017) that the thermal degradation of vitamin C fits the first-order kinetic model in different dried foods.

Air-drying may have a negative effect on the physical properties of products and cause degradation of aromatic

Table 4. Color properties of goji berry fruits.

	L^*	a^*	b^*	ΔE
Fresh	25.97 ± 0.12 ^a	25.16 ± 0.13 ^a	17.30 ± 0.05 ^a	
50°C	23.11 ± 0.09 ^b	16.45 ± 0.07 ^b	11.03 ± 0.11 ^b	10.87
60°C	22.79 ± 0.05 ^c	14.41 ± 0.09 ^c	10.67 ± 0.07 ^c	13.01
70°C	21.99 ± 0.06 ^d	14.67 ± 0.08 ^d	9.62 ± 0.05 ^d	13.91

*Different letters in the same column are significantly different values ($P < 0.05$).

compounds and nutrients (Araya-Farias *et al.*, 2011). In other words, losses are observed in the compounds found in all foods, especially vitamin C, by heat treatment. Dağhan *et al.* (2018) studied the hot air drying of Isot at different temperatures and found that there was significant loss in vitamin C. They found the highest loss at 75°C and stated that vitamin C is highly sensitive to changes in temperature. Marfil *et al.* (2008) performed tomato hot air drying at different temperatures and reported that the loss of vitamin C in tomatoes increased with increase in drying temperature. Kinetic parameters of vitamin C in goji berries are presented in Table 5. Vitamin C degradation rate constants of goji fruits at 50°C, 60°C, and 70°C were found to be 0.047, 0.075, and 0.182 1/h, respectively. It is clearly observed that the rate constant increased but

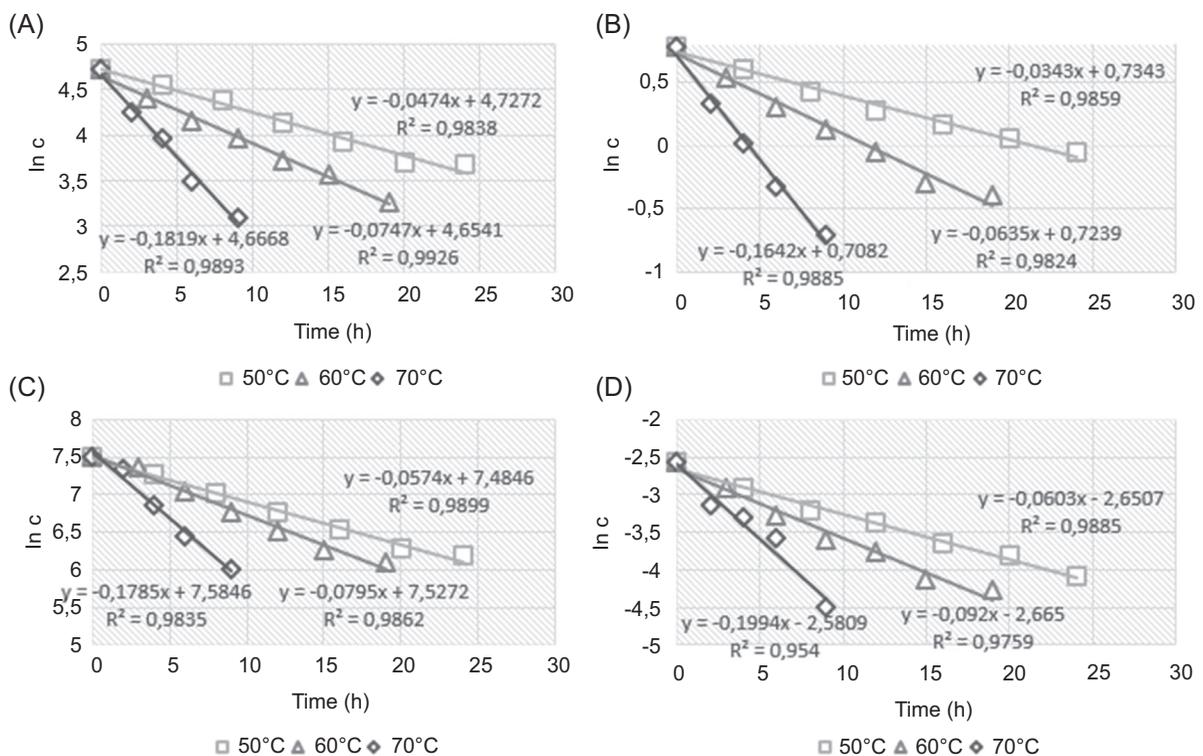


Figure 3. First-order kinetics of (A) vitamin C, (B) pyridoxine, (C) total phenolic content (TPC), and (D) antioxidant capacity (AC) of goji berries.

Table 5. First-order kinetic parameters of vitamins C and B₆, total phenolic content, and antioxidant capacity of dried goji berries.

Compound	Temperature	k	$t_{1/2}$	D	R^2	E_a	E_a	Q_{10}	Q_{10}
		(1/h)	(h)	(h)		(kcal/mol)	(kJ/mol)	(50–60°C)	(60–70°C)
Vitamin C	50°C	0.047	14.62	48.59	0.984	14.75	61.72	1.58	2.44
	60°C	0.075	9.28	30.83	0.993				
	70°C	0.182	3.81	12.66	0.989				
Pyridoxine (vitamin B ₆)	50°C	0.034	20.2	67.14	0.986	17.19	71.94	1.85	2.59
	60°C	0.064	10.91	36.27	0.982				
	70°C	0.164	4.22	14.03	0.989				
TPC	50°C	0.057	12.07	40.12	0.990	12.43	52.01	1.39	2.25
	60°C	0.080	8.72	28.97	0.986				
	70°C	0.179	3.88	12.90	0.984				
AC	50°C	0.060	11.49	38.19	0.989	13.12	54.90	1.53	2.17
	60°C	0.092	7.53	25.03	0.976				
	70°C	0.199	3.48	11.55	0.954				

TPC, total phenolic content; AC, antioxidant capacity.

$t_{1/2}$ and D values of vitamin C decreased due to the increment in temperature. Similarly, Demiray *et al.* (2013) stated that the k value increased with the increment in drying temperature. They also stated that the $t_{1/2}$ value decreased with the increase of drying temperature in drying of tomatoes. Kadakal *et al.* (2017) stated that the degradation rate constant of vitamin C was increased due to the thermal increase in rosehip nectar while the $t_{1/2}$ and D values were decreased. Our results are compatible with literature. Also, the Q_{10} value from 60°C to 70°C was found to be higher than from 50°C to 60°C. With this data obtained in our study, it is understood that the thermal degradation of vitamin C is more sensitive to the increment of temperature from 60°C to 70°C. The Q_{10} value of vitamin C thermal degradation increased with the decrement in drying temperature (Demiray *et al.*, 2013; Kadakal *et al.*, 2017). Kadakal *et al.* (2017) stated that high activation energy of reaction indicates that the reaction sensitivity of temperature is very high. The Arrhenius equation of vitamin C thermal degradation is given in Figure 4.

To the best of our knowledge, the degradation of vitamin B₆ in the hot air-drying process in goji berries has been investigated for the first time. Thermal degradation of vitamin B₆ is shown in Figure 3, and the kinetic parameters of vitamin B₆ thermal degradation are presented in Table 5. The thermal degradation of vitamin B₆ content in fully dried goji berries is found to fit the first-order kinetic model. Vitamin B₆ degradation rate constants of goji berries at 50°C, 60°C, and 70°C have been found to be 0.034, 0.064, and 0.164 1/h, respectively. Rate constant increased, but the $t_{1/2}$ and D values of vitamin B₆

decreased due to the increment in temperature. Kadakal *et al.* (2017) stated that the degradation rate constant in vitamin B complex increased due to thermal increase in rosehip nectar. Also, the Q_{10} value from 60°C to 70°C was found to be higher than that from 50°C to 60°C. When Q_{10} values vitamins C and B₆ were compared, it was understood that vitamin B₆ is more sensitive to increase in temperature. The E_a value of vitamin B₆ was found to be 71.94 kJ/mol. When the E_a values of vitamins C and B₆ were compared, the E_a value of vitamin B₆ was higher than that of vitamin C, which means that vitamin B₆ is more stable than vitamin C. At the same time, vitamin B₆ is more sensitivity to changes in temperature than vitamin C.

Kinetic parameters of total phenolic content and antioxidant capacity

There are no data about the kinetic parameters of TPC in dried goji berries. The TPC thermal degradation is shown in Figure 3, and the kinetic parameters of TPC thermal degradation are listed in Table 5. The TPC thermal degradation rate constant increased and values of $t_{1/2}$ and D decreased with the increment in drying temperature. Thermal degradation of TPC content in fully dried goji berries was found to fit the first-order kinetic model. The rate constant of TPC thermal degradation in goji fruits ranged from 0.057 to 0.179 1/h. TPC thermal degradation increases depending on the increment of temperature (Kadakal and Duman, 2018; Sarpong *et al.*, 2018). López *et al.* (2010) reported that the TPC value decreased with increase in the temperature of drying air. The activation

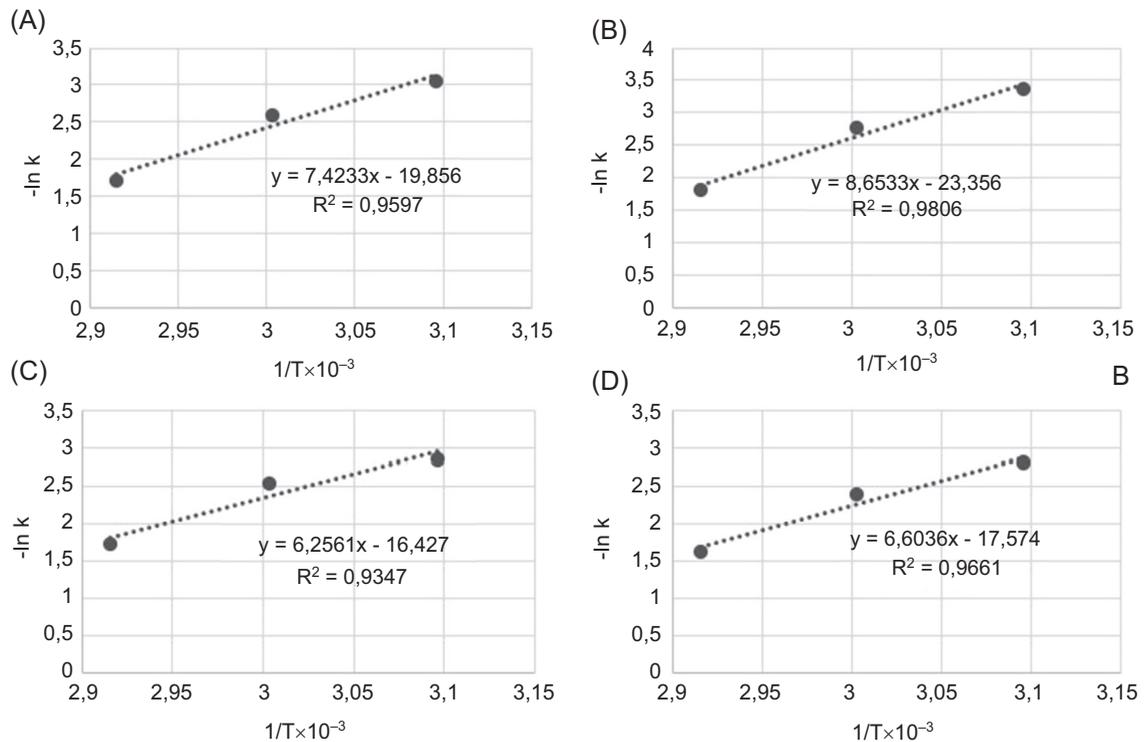


Figure 4. Arrhenius plots of dried goji berries: (A) vitamin C, (B) pyridoxine, (C) total phenolic content (TPC), and (D) antioxidant capacity (AC).

energy was calculated using the Arrhenius equation presented in Figure 4 and found to be 52.01 kJ/mol. The Q_{10} value from 60°C to 70°C was found to be higher than that from 50°C to 60°C. Thus, the thermal degradation of TPC is more sensitive to the increment of temperature from 60°C to 70°C.

To the best of our knowledge, AC thermal degradation in dried goji fruits was studied for the first time in the current study. The AC thermal degradation is shown in Figure 3, and the kinetic parameters of AC thermal degradation are given in Table 5. In the current study, thermal degradation of AC in fully dried goji berries was found to fit the first-order kinetic model. Oancea *et al.* (2017) used the first-order kinetic model on AC thermal degradation in sour cherry extract. Owing to temperature increment, the rate constant increased but $t_{1/2}$ and D values of AC decreased. Oancea *et al.* (2017) and Sarpong *et al.* (2018) reported that the rate constant of AC increased with increase in temperature in sour cherry extract and banana slices, respectively. The Arrhenius equation of AC thermal degradation is presented in Figure 4 and E_a was found to be 54.90 kJ/mol. The Q_{10} values from 50°C to 60°C and from 60°C to 70°C were found as 1.53 and 2.17, respectively. In this context, the increment in Q_{10} value from 60°C to 70°C indicates that the thermal degradation of AC is more sensitive than that in the range of 50–60°C.

Conclusions

In this study, for the first time, drying characteristics and thermal degradation of some ingredients in goji berry (*Lycium barbarum* L.) grown in Turkey were investigated under different drying conditions. Page model was determined to be the best model to predict experimental moisture ratio at all drying temperatures (50°C, 60°C, and 70°C). Drying temperature affects the drying speed and drying time. Drying time ranged from 9 to 24 h at 50–70°C. With increase in drying temperature, effective moisture diffusivity increased and the highest effective moisture diffusivity was determined at 70°C. The drying process showed losses in vitamins C and B₆, TPC, and AC, and the highest loss was observed at 70°C. The highest percentage loss was found in AC. The thermal degradation of Vitamins C and B₆, TPC, and AC is found to fit the first-order kinetic model, and the drying rate values of all these in goji berries increased by drying temperature increment. Vitamins C and B₆ were very susceptible to temperature increment, but TPC and AC were the lowest sensitive compounds in dried goji berries. The highest color difference (ΔE) was obtained in the goji berries dried at 70°C. The shortest drying time was observed in the goji berries dried at 70°C, and the drying process at 50°C provided the highest retention of bioactive compounds in goji berries. According to the data obtained and evaluated,

the optimal drying temperature for goji berries is 50°C in hot air drying.

As additional studies, research should be conducted on obtaining dried goji berries with different and combined drying method, which could be a more efficient drying process with less component loss. Also, the content differences in goji berries grown at different locations should be investigated.

Acknowledgments

This study was supported by Pamukkale University with grant number 2018FEBE026.

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